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Organic matter reactivity indicators in sediments of the St. Lawrence Estuary

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ABSTRACT

Here we report multiple parameters used to describe the diagenetic state of sediments, including total hydrolyzable amino acid (THAA), amino acid enantiomer, chlorin (CI) and amino acid degradation (DI, RI) indices, along a transect between the Upper St. Lawrence Estuary and the Gulf of St. Lawrence, Canada. The study area is characterized by gradients in water oxygen concentration, water depth, organic matter (OM) source, primary productivity, and sedimentation rate. Both CI and DI indicate a decline in OM reactivity, with the transition from a more terrestrial to a more marine-dominated sedimentation regime as one moves from the shallow Upper Estuary (23–95 m) to the hypoxic, mid-depth Lower Estuary and to the deep (>400 m), well-oxygenated Gulf. Whereas the CI more accurately reflected OM reactivity in surface sediments and sediments down to 5 cm, the amino acid-based degradation indices (DI and RI) better described degradation in sediments down to 35 cm. Systematic variations in the amino acid composition along the Laurentian Channel confirmed the increased diagenesis of OM with distance from the Upper St. Lawrence Estuary. The ratio of D/L-stereoisomers of alanine increased along the transect, and the co-variation between DI and the D/L-Ala suggest a close coupling between the extent of diagenesis and the accumulation and selective preservation of bacterially-derived cell wall material in the sediments. The same patterns that we observed along the estuarine transect were present down-core in two sediment cores, confirming the robustness of our reactivity indices. Oxygen exposure time of the sediments appears to strongly determine sediment OM reactivity in the St. Lawrence Estuary. The sediment oxygen regime itself is related to the interplay between water column depth, vertical OM flux, and reactivity of settling OM.

1. Introduction

The susceptibility of individual components of particulate organic matter (OM) to degradation during transport and burial in estuarine sediments under variable depositional conditions has long been discussed (e.g., Burdige, 2007; Niggemann et al., 2007). Key factors that influence particulate OM degradation and preservation include water column depth, redox conditions, particulate OM fluxes, sedimentation rate, sediment physical properties and microbial activity. The latter depends mainly on the nutritional quality and availability for microbes, generally defined as the OM bioreactivity (Gray et al., 2002). There is no single explanation for what exactly controls the turnover of bulk OM in general, and single components in particular, in estuaries (Hopkinson and Smith, 2005). The coincidence of spatial variations of several environmental factors can make it very difficult to separate the influence of individual factors at any given location.

The origin of the OM supplied to the sediments is one of the main factors that determines the composition and reactivity of sedimentary OM (Burdige, 2007). Whereas the production and degradation of autochthonous OM occurs entirely within the marine environment, terrestrial OM is produced and transported on land and may already be significantly altered before entering the marine system (Hedges and Keil, 1995). Shifts in the relative importance (marine vs. terrestrial) of the particulate OM flux at the sediment surface may influence OM reactivity and degradation in sediments. The general perception is that terrestrially-derived OM is rather recalcitrant. As a consequence, sediments dominated by

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terrestrial inputs can be expected to be less reactive than sediments that contain mostly autochthonous algal OM, at least if early diagenetic processes are of secondary importance.

Another factor that influences sedimentary OM diagenesis is the local redox condition. The efficiency of different respiration pathways (e.g., oxic vs. anoxic) with regards to the rates and degree of OM degradation has been investigated in laboratory experiments and the field (e.g., Lehmann et al., 2002; Pantoja et al., 2009). Furthermore, bulk organic carbon (C) preservation has been shown to be directly related to the oxygen exposure time of sinking and settling particles (Hartnett et al., 1998; Hedges et al., 1999), and redox oscillations have been found to enhance OM degradation largely by promoting symbiosis of aerobic and anaerobic microorganisms (Aller, 1994).

A major challenge in our understanding of OM dynamics in estuarine sediments is the actual description and quantification of the diagenetic state or reactivity of the sedimentary OM pool. Generally, bulk descriptors of sediments such as organic carbon content or carbon-to-nitrogen atomic ratio, explain little of the variation in benthic heterotrophic OM degradation rates at neither local nor regional scale (Zimmerman and Canuel, 2001; Hopkinson and Smith, 2005). Therefore, a number of bioindicators have been proposed to determine the relative degradation state of OM (e.g., Cowie and Hedges, 1994; Dauwe et al., 1999; Schubert et al., 2005). In particular, protein amino acids (AA) and chlorins (i.e., chlorophyll and its early degradation products), have been used as indicators for the overall state of OM degradation (Dauwe et al., 1999; Schubert et al., 2005). Also, the relative abundance (mole %) of the non-protein amino acids β-Alanine (BALA) and γ-Aminobutyric acid (GABA) increases as OM is degraded, thus providing additional information on the degradation state of total OM (Cowie and Hedges, 1994; Keil et al., 2000).

Other diagenetic indicators are directly related to microbial processes in the sediments. Bacterial cell death produces bacterial remnants consisting of a variety of components that have variable susceptibilities towards degradation (Lomstein et al., 2009). One of the more refractory components is peptidoglycan, a unique constituent of bacterial cell walls containing D-amino acids (Grutters et al., 2002). D-AAs in aquatic systems, usually reported relative to their respective ubiquitous L-stereoisomers as D/L-AA ratios can thus be used as indicator of bacterial biomass (Grutters et al., 2002; Veuger et al., 2005). Indeed, the D-alanine to L-alanine (D/L-Ala) ratio of sediments generally increases during early diagenesis as bacterially produced OM accumulates (Lomstein et al., 2006, 2009).

These various indices of sedimentary OM target related but distinct facets of sediment OM quality and diagenetic state, and most likely provide complementary information. Yet the links that exist between them, and with other environmental factors, are still not well understood. The Laurentian Channel of the Saint Lawrence Estuary (Fig. 1) displays pronounced spatial variations in OM source, water column depth, surface water productivity, and water column DO concentration, and hence provides an excellent test case to study the environmental controls on sediment OM reactivity. In this study we combined the indicators described above, with bulk chemical and isotopic measures of sediment OM, to explore patterns in diagenetic state of the OM along the St. Lawrence Estuary and their links to OM sources and depositional regime.

2. Sampling and methods

2.1. Study site and sampling

The Lower St. Lawrence Estuary and the Gulf form a semi-enclosed sea connected to the Atlantic by the south–eastern Cabot Strait (Fig. 1). The estuary is divided into the Lower Estuary and the Upper Estuary near the mouth of the Saguenay Fjord, where average water depth drops suddenly from ~100 m to ~300 m. The morphology of the Lower Estuary and the Gulf is dominated by the Laurentian Channel, a 1200 km long submarine canyon that stretches from the mouth of the Saguenay Fjord through the Gulf of St. Lawrence and the Cabot Strait to the edge of the continental shelf.

The Upper Estuary is characterized by extremely low net sedimentation, with less than 10% of its total surface area covered with fine sediment deposits (d'Anglejan, 1990). On an average, the suspended particulate matter load discharged by the St. Lawrence River to the Lower Estuary and the Gulf of the St. Lawrence amounts to 6.5×10^6 t yr^{-1} (Rondeau et al., 2000). The Lower Estuary is

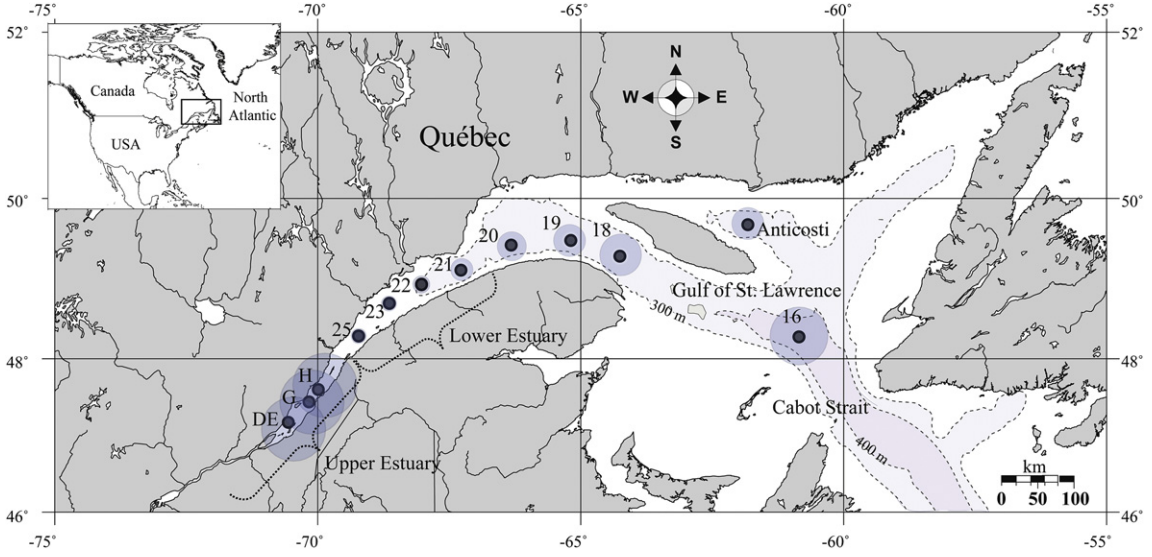

Fig. 1. Map showing the sampling locations in the St. Lawrence estuary (upper and lower) and the Gulf of St. Lawrence. Bathymetric contours outline the Laurentian channel along the 300 and 400 m isobaths. The size of shadowed circles around study sites denotes bottom water DO concentrations. For absolute values of bottom water DO see Table 1.